

The chlorine budget of the lower polar stratosphere: Upper limits on ClO, and implications of new Cl₂O₂ photolysis cross sections

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Abstract. Chlorine catalytic chemistry, which destroys ozone while cycling chlorine between Cl, ClO, and Cl₂O₂, is the primary cause of the springtime Antarctic ozone hole. We have calculated the concentrations of Cl₂O₂ which are in equilibrium with midday ground-based, aircraft, and satellite observations of ClO in the Antarctic spring lower stratosphere. Two significant conclusions are presented here: (1) Using the JPL 94 recommended rates and photolysis cross sections, more than ~2.0 ppbv ClO in the polar lower stratosphere causes inferred total active chlorine to exceed the total chlorine budget. This limit is smaller than some reported ClO measurements. (2) Using smaller cross sections recently measured by Huder and DeMore [1995], the amount of Cl₂O₂ in midday equilibrium with measured ClO is approximately doubled. Activated chlorine inferred from many measurements then exceeds total chlorine in the lower stratosphere, suggesting these cross sections may be too small.

Introduction

Breakdown of chlorofluorocarbons (CFCs) in the stratosphere releases inorganic chlorine which is the primary agent responsible for the annual Antarctic 'ozone hole' [e.g. Solomon, 1990]. Heterogeneous chemistry transfers inorganic chlorine into large concentrations of chlorine monoxide (ClO) in the lower stratosphere, and the chlorine monoxide dimer (Cl₂O₂) catalytic cycle [Molina and Molina, 1987] is then responsible for the majority of Antarctic ozone depletion. In this paper, we place limits on the maximum amounts of midday ClO that can be accommodated within the total estimated chlorine budget of the stratosphere, using the current recommended dimer photolysis cross sections that govern the partitioning of Cl between ClO and its dimer. We also point out that many existing midday measurements of ClO are inconsistent with the total chlorine budget if the new ClO dimer photolysis cross sections proposed by Huder and DeMore [1995] are employed.

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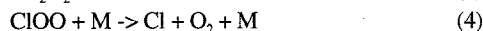
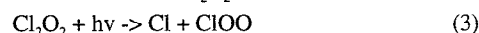
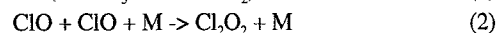
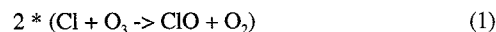
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Chlorine Chemistry Overview

During the polar winter, heterogeneous reactions on PSCs rapidly convert chlorine from HCl and ClONO₂ into Cl₂, HOCl, and ClNO₂, which are then photolyzed to yield atomic chlorine after polar sunrise. Atomic chlorine itself reacts very rapidly, so that the dominant chlorine species immediately become ClO and Cl₂O₂. The heterogeneous reactions proceed so quickly that most, if not all, chlorine in the reservoir species is converted into active chlorine well before polar sunrise. We will assume here that all available inorganic chlorine was first heterogeneously activated, and then converted into ClO and its dimer after polar sunrise, leaving no chlorine present in reservoir species.

The ozone-destroying catalytic cycle of concern here is:



The partitioning of chlorine monoxide between ClO and Cl₂O₂ is governed by reactions 2 and 3. These reactions are very rapid, and even the relatively low intensity of sunlight during the early Antarctic spring is sufficient to maintain equilibrium between ClO and Cl₂O₂ during the midday period. The equilibrium concentration of Cl₂O₂ is then given by:

$$[\text{Cl}_2\text{O}_2] = \frac{k_2[\text{ClO}]^2[\text{M}]}{k_{2R}[\text{M}] + J_3} \quad (5)$$

where k_2 and k_{2R} are the forward and reverse rate constants of reaction 2, J_3 is the rate constant of reaction 3 (dimer photolysis), and square brackets represent concentration.

Since photolysis rates are a key issue, we have been careful in our calculations to match conditions present during the Antarctic ozone hole period. The solar flux is calculated in a spherical atmosphere using a delta-Eddington technique which is known to be accurate at very high solar zenith angles, and in the presence of a high polar surface albedo, as outlined in Shindell and de Zafra [1995]. Overlying ozone and oxygen are treated as absorbers, using local balloon observations up to about 32 km altitude (B. Johnson, private communication), and Microwave Limb Sounder (MLS) data for O₃ at higher altitudes (J. Waters, private communication). Temperature is taken from the balloon soundings as well.

The Total Chlorine Budget

The photolytic breakdown of organic chlorine source gases into inorganic chlorine is incomplete in the lower

stratosphere. Source gas measurements taken within the northern polar vortex during 1992 yielded ~ 3.2 – 3.4 ppbv total chlorine, and a maximum of about 3.1 – 3.2 ppbv inorganic chlorine near 20 km altitude [von Clarmann *et al.*, 1995; Woodbridge *et al.*, 1995]. We assume that 1993 values would be approximately 0.1 ppbv larger, based on a 2.8%/yr increase in emissions [World Meteorological Organization, 1991]. The substantial descent which takes place within the polar vortex during winter is approximately 2–4 kilometers less near 20 km altitude in the southern hemisphere than in the northern [Rosenfield *et al.*, 1994]. To compensate, we have shifted the northern hemisphere data upwards 3 kilometers at 20 km altitude, and somewhat less at lower altitudes.

Results

A number of measurements of Antarctic midday ClO abundance are available. For illustrative purposes, we first consider a set of ground-based mm-wave measurements, which fall in the mid-range of other measurements. We have made a series of observations of the day-minus-predawn value of ClO during September and early October 1993 [de Zafra *et al.*, 1995]. Since a small amount of ClO is present at night, unconverted to the dimer (see Shindell and de Zafra, 1995), we have performed a simple model calculation of the day-night cycling between ClO and Cl_2O_2 to derive the predawn residual abundance of ClO. This was then used to convert midday-minus-predawn measurements derived from differencing of spectra to slightly larger midday values.

In the upper left panel of Figure 1 we show the midday mixing ratio of ClO versus altitude from our September 4–7, 1993 data, the Cl_2O_2 mixing ratio calculated for September 6, 1993 conditions over McMurdo Station using Equation 5, and the total $\text{ClO} + 2^*\text{Cl}_2\text{O}_2$ in the lower stratosphere. For this illustration, the rate constants for reactions 2 and 2R, as well as the photolysis cross sections of Cl_2O_2 , were taken from the 1994 JPL evaluation [DeMore *et al.*, 1994]. In the lower left panel we show the same quantities when the dimer abundance has been calculated using the new photolysis cross sections of Huder and DeMore [1995]. Similar results are shown for September 30 conditions (smaller solar zenith angle, warmer temperatures) in the two righthand panels, using our data averaged over September 30 to October 1. The ClO layer has descended, as discussed in de Zafra *et al.* [1995], leading to greater Cl_2O_2 abundances at lower altitudes. We note that our measurements recover profiles only down to 16 km due to the spectral bandpass limit. Values below this level result from the initializations used in the data retrieval process, which are based on polar aircraft observations [Brune *et al.*, 1989; as corrected in Anderson *et al.*, 1991]. Data are shown at 14 km only to illustrate the vertical extent of the ClO layer.

We also show the total chlorine and the inorganic chlorine loading in the lower stratosphere from von Clarmann *et al.* [1995] and Woodbridge *et al.* [1995] (modified as discussed in the previous section). The total active chlorine required by use of the Huder and DeMore cross sections, shown in the lower panels, is significantly larger than the inorganic chlorine, as well as even the total available chlorine, though within or near the limit of the rather large uncertainty in the inferred total active chlorine abundance.

Satellite ClO measurements from the MLS [Waters *et al.*, 1993] have indicated peak mixing ratios in the range of 2.0–2.5 ppbv for the 1992 Antarctic lower stratosphere at 46 hPa (~ 19 km). ClO mixing ratios this large result in $\text{ClO} + 2^*\text{Cl}_2\text{O}_2$ amounts which are larger than the available chlorine, as indeed pointed out by Waters *et al.* [1993]. For the conditions present over McMurdo during early September 1993 (at 46 hPa, $T \sim 190$ K), active chlorine inferred by our model from 2.1 ppbv ClO is greater than 4 ppbv, and from 2.5 ppbv ClO is ~ 6 ppbv (note the quadratic dependence of Cl_2O_2 on ClO in Equation 5), much greater than any estimate of total available chlorine. Use of the reduced Huder and DeMore cross sections only exacerbates this disagreement.

In situ measurements of ClO were made from an ER-2 aircraft within the lower part of the Antarctic vortex on several occasions in 1987 [Anderson *et al.*, 1991]. These measurements yielded maximum mixing ratios of about 1.2 ppbv in mid-September at the aircraft's altitude limit of ~ 18.5 km. These measurements would imply a 1993 value of about 1.5 ppbv, assuming an increase of about 3%/year in chlorine loading, and the same total activation as in 1993. In Emmons *et al.* [1995], we reported peak ClO mixing ratios within the Antarctic vortex of about 1.2 ± 0.3 ppbv from 1987 data after use of an improved retrieval method, which again is equivalent to about 1.5 ppbv for 1993 chlorine loading. The same paper gives a measurement of about 1.6 ppbv for 1992.

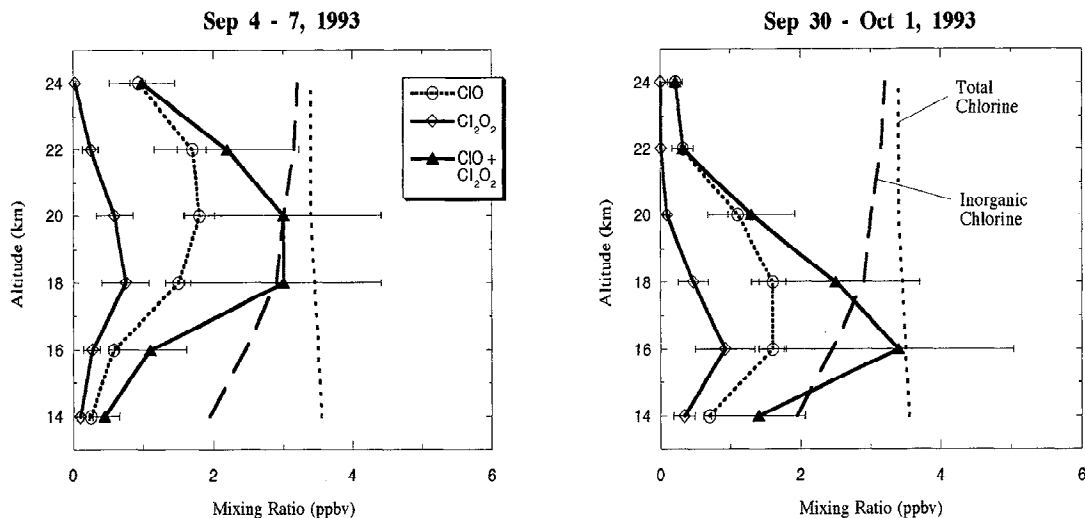
In summary, midday ClO maximum values of ~ 1.6 – 1.9 ppbv yield inferred active chlorine amounts, using the JPL 94 recommended cross sections and rate constants, at or near the total available inorganic chlorine level, indicating roughly the maximum amount of ClO which is consistent with the total chlorine budget, assuming there has been complete conversion of chlorine into active forms. Note that any chlorine remaining in reservoir species would make agreement with total chlorine worse, not better. We conclude that all of the existing ground-based and aircraft measurements are consistent with total contemporaneous chlorine loading and the recommended dimer photolysis cross sections in the 1994 JPL compilation. The results are highly suggestive that these measurements are not in agreement with the new data of Huder and DeMore [1995]. ClO mixing ratio measurements of more than ~ 2.0 ppbv cause inferred active chlorine to significantly exceed inorganic chlorine with either value of dimer photolysis cross sections.

Discussion of Uncertainties

There is some uncertainty in the amount of total inorganic chlorine available in the lower stratosphere. Woodbridge *et al.* [1995] give an uncertainty of $\sim 6\%$ on Cl_y , while the results of von Clarmann *et al.* [1995] yield a value of $\sim 14\%$. We emphasize again that any residual Cl remaining in the reservoir species HCl and ClONO_2 means that this amount must be added to the amount of chlorine present in ClO and Cl_2O_2 , making the discrepancies even larger.

The uncertainty quoted in the 1994 JPL evaluation for the dimer formation rate constant at 190 K is $\pm 50\%$. We have recently suggested [Shindell and de Zafra, 1995] that this range can be reduced to $\pm 30\%$ using the observed diurnal variation of

JPL 94 Cross Sections



Huder and DeMore Cross Sections

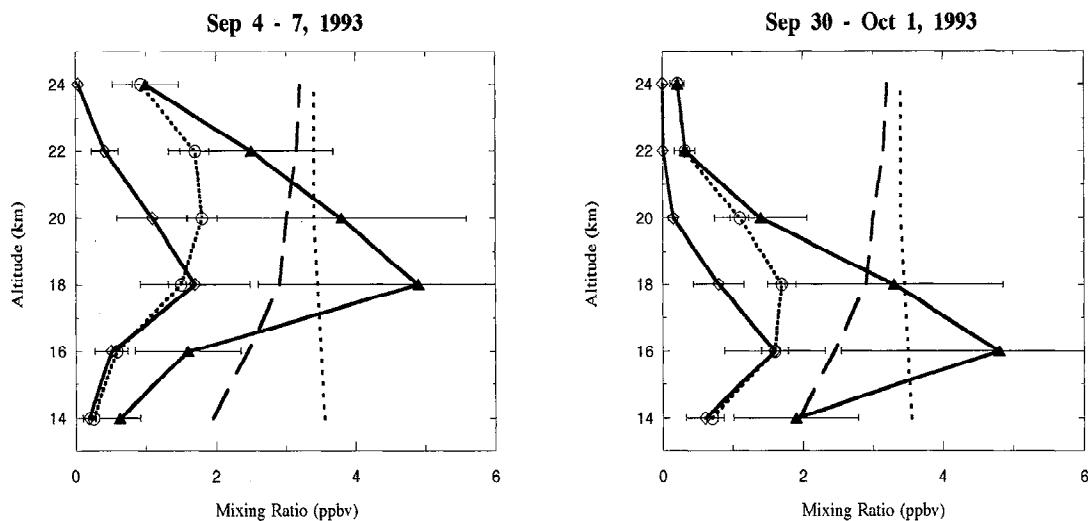


Figure 1. The four panels show midday ClO measurements averaged over September 4-7, 1993 and September 30-October 1, 1993 from McMurdo Station, Antarctica. Equilibrium mixing ratios of Cl₂O₂ and the total inferred active chlorine are shown as well. The upper panels display results calculated using the JPL 94 Cl₂O₂ photolysis cross sections, while the cross sections of *Huder and DeMore* [1995] have been used in the lower panels. The rightmost dotted line indicates the total estimated chlorine loading in the polar lower stratosphere, while the dashed line gives the upper limit on the amount of inorganic chlorine, both as given by *von Clarmann et al.* [1995] and *Woodbridge et al.* [1995] (modified as discussed in the text, uncertainty of $\leq 14\%$). See text for full discussion of uncertainties.

ClO in the Antarctic stratosphere. The value and uncertainty we obtain are similar to the those obtained in the laboratory studies of *Nickolaissen et al.* [1994], and *Trolier et al.* [1990], and we believe these three studies have established a reliable rate constant and uncertainty limits for the dimer formation reaction. We have therefore used the JPL 94 value, but with an uncertainty of $\pm 30\%$ here. The contribution from the uncertainty in the thermal dissociation rate constant is negligible at midday, as the denominator in Equation 5 is dominated by the rapid midday photolysis rate. We have taken the uncertainty in the photolysis cross sections to be $\pm 25\%$, as the JPL 94 values are based on four data sets which are within

10-35% of each other depending on wavelength. The results presented here depend on the photolysis rate calculation at midday only. The uncertainty in this calculation is therefore small compared the other uncertainties ($< 5\%$).

The above uncertainties in the rate constants and photolysis cross sections, as well as an uncertainty of $\pm 12\%$ (1 sigma) in the ClO measurements, have been used to derive a mixing ratio uncertainty for Cl₂O₂ of $\pm 46\%$, which has been added in quadrature with the ClO measurement uncertainty to give the $\pm 48\%$ uncertainty for total activated chlorine shown in Figure 1. (We note that no uncertainties were given by *Huder and DeMore* [1995], so we have again used $\pm 25\%$ photolysis cross

section uncertainty.) The results are clearly suggestive that using the *Huder and DeMore* cross sections, the total active chlorine does not agree with the total chlorine budget.

Additional chemical or photolytic processes are also a consideration. A new mechanism for dimer loss during the day could reduce the budget problem, however likely pathways seem to be too slow. The reaction of the dimer with Cl is only about 1% as fast as photolysis, and reactions with O or O₃ are even slower. The possible yield of two ClO molecules from dimer photolysis discussed by *Huder and DeMore* [1995] would only make matters worse, as would any additional as yet unknown chlorine chemistry which might yield a new chlorine reservoir. Furthermore, any attenuation of radiation by aerosols or PSCs would reduce the photolysis rate of the dimer, exacerbating the chlorine budget problem.

Summary

We have calculated the total amount of active chlorine as a function of altitude within the Antarctic spring lower stratosphere using measurements of ClO and the derived equilibrium amount of Cl₂O₂. Using the JPL 94 recommended rates and cross sections to derive the midday equilibrium dimer amount, measurements of ~1.6-1.9 ppbv ClO in the 1993 Antarctic vortex result in inferred total active chlorine levels (ClO + 2 * Cl₂O₂) that are at or near the inorganic chlorine loading of the Antarctic stratosphere, even assuming virtually complete conversion of available inorganic chlorine into active forms. These results imply that mixing ratios of ClO in excess of 2.0 ppbv are inconsistent with the amount of inorganic chlorine available in the polar lower stratosphere (though the uncertainty on inferred active chlorine is considerable). Using the dimer photolysis cross sections recently measured by *Huder and DeMore*, we derive total abundances of activated chlorine in the 4-5 ppbv range, greatly exceeding the amount of inorganic or even total chlorine available in the lower stratosphere. This discrepancy is present using measurements taken during both early and late September under rather different photolysis conditions. We suggest that further measurements of the dimer photolysis cross sections are needed to resolve this issue.

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